

## Atmospheric reactivity of Biofuel

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Concerns related to climate change and energy security has led to a substantial increase in the global production of biofuels over the past decade. Fatty acid methyl esters (FAMEs) made from transesterification of plant oils or animal fats are the dominant biofuel in the EU. The widespread use of FAMEs in diesel blends will lead to their release into the atmosphere. It is therefore essential to know the atmospheric impact of any potential biofuel. The main atmospheric loss process is reaction with hydroxyl (OH) radicals.

We will consider the atmospheric degradation of esters  $\text{CH}_3(\text{CH}_2)_x\text{C}(\text{O})\text{O}(\text{CH}_2)_y\text{CH}_3$  (where  $x=0,1,2,3$  and  $y=0,1,2,3$ ) which serves as model compounds for biofuel (1-4). The OH radical abstracts a hydrogen atom from the ester and often there are several sites for H-abstraction. Each H-abstraction site leads to different reaction products. It is important to know the branching ratio between the different H-abstraction channels in order to predict which biofuel compound has the least environmental impact. There is a great interest in discovering the underlying factors causing these unexpected reactivities, which is likely to involve reactant and product complexes.

In this presentation we will study the hydrogen abstraction reaction mechanism between esters and OH radical using electronic structure theory. We will estimate the branching ratio of different reaction channels.

For example for methyl acetate  $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ , the probability that the OH radical abstracts a hydrogen atom of the  $-\text{OCH}_3$  group is predicted to be greater than 90 % (1-2). This reaction channel dominates since both the structures of the reactant complex and the transition state are stabilized by three H-bonds, forming a seven member ring-like structure. We also investigated the reaction of OH radicals with the two  $\text{C}_4\text{H}_8\text{O}_2$  isomers; methyl propionate ( $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3$ ) and ethyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ ) (3). In ethyl acetate the H-abstraction was computed to occur exclusively (~99%) at the  $-\text{OCH}_2-$  group (3). In contrast, both methyl groups and the  $-\text{CH}_2-$  group contribute appreciably in the reaction of OH with methyl propionate. In general H-abstraction from the  $-\text{C}(\text{O})\text{OCH}_2-$  dominates and only in the case of methyl esters ( $\text{R} = \text{CH}_3$ ) does H-abstraction from the beta carbon position of  $-\text{CH}_2\text{CH}_2(\text{O})\text{OR}$  dominate.

### References

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